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The determination of the infrared radiative lifetimes of a vibrationally excited neutral molecule using stimulated-emission-pumping, molecular-beam time-of-flight

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The authors present a new experimental method for measurement of collision-free infrared radiative lifetimes for single quantum states of a vibrationally excited sample. This method provides a more direct route to the infrared Einstein A coefficients than has been previously possible. Results for NO($X\ ^2\Pi$, $v=21$ and $v=7$) are presented. Comparison to results of *ab initio* calculations shows excellent agreement. A controversy regarding the relative intensities of first overtone and fundamental emission intensities in NO is laid to rest. The most complete least squares analysis of existing data was carried out to derive the electric dipole moment function (EDMF) to an accuracy of ± 0.02 D between 0.9 and 1.7 Å. © *1997 American Institute of Physics.*
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INTRODUCTION

The use of infrared emission has a long and rich history in the study of chemical reaction dynamics,[1–4] spectroscopy,[5,6] and chemical lasers.[7,8] Quantitative experiments rely on a knowledge of the Einstein A coefficients which characterize the rate of spontaneous emission. Well established techniques exist for the determination of such coefficients for $v=1\rightarrow 0$ for simple molecules, however as the vibrational quantum numbers increase, measurements become more difficult. Up to now, the basic strategy involves first finding quantitative absorption strengths for the fundamental $1\leftarrow 0$ transitions and as many overtones as possible. In combination with vibrational-state-specific dipole moments, often available from microwave spectroscopy, this allows the construction of the electric dipole moment as a function of internuclear separation, EDMF. Additional experimental data such as the ratio of fundamental to overtone emission in nonequilibrated and highly vibrationally excited samples can be used to constrain the EDMF at larger internuclear separations. Once an accurate EDMF has been obtained, the calculation of Einstein A coefficients is possible from theory.[9–12]

The observation of infrared emission from NO in the upper atmosphere especially during auroral events[13] has shown the presence of high vibrational states[14,15] and has motivated attempts to determine the infrared Einstein A coefficients for a wide range of v. *Ab initio* calculations of the EDMF have been carried out and used to give the A coefficients up to $v=20$ and $J=33.5$.[16–18] Measurements of the first overtone-to-fundamental intensity ratio in chemiluminescence experiments were found to increase up to $v=11$ and then decreased,[19] casting doubt on the theoretical EDMF. Higher levels of *ab initio* theory have recently been reported,[20] which agree well with the earlier theoretical work. They predict the first overtone-to-fundamental intensity ratio to continue to increase above $v=11$ and to approach unity at $\sim v=20$.

For NO and other molecules, present methods are indirect. That is, intensity information is used to derive kinetic rate coefficients. Due to the indirect nature of the process, the analysis relies on the quality of a large data base of emission and absorption strength measurements. Artifacts appearing in parts of the data base will introduce error to the determination of the EDMF and this error may propagate to all of the derived A coefficients. For excited electronic states undergoing visible or ultraviolet emission, the determination of Einstein A coefficients is commonly accomplished by measurements of the collision free radiative lifetime. Remarkably, a method designed for direct observation of the rate of *infrared* radiative relaxation has not been established. Such a measurement would first require efficient preparation of vibrationally excited molecules. In this paper an approach is presented employing stimulated emission pumping[21,22] (SEP), an optical pumping method which is capable of producing large concentrations of highly vibrationally excited molecules in single quantum states. SEP is a folded variant of optical–optical double resonance and uses two laser pulses to excite molecules out of thermally populated levels into highly vibrationally excited states through an intermediate electronically excited state. The large structure change upon electronic excitation in many molecules allows good Franck–Condon overlap to high vibrational states in the two-photon transition. For example, NO($X\ ^2\Pi_\Omega$) can easily be produced in excited states up to $v=25$.[23]

In addition to efficient optical pumping, the direct measurement of infrared Einstein A coefficients requires the ability to probe the time dependence of the population under collisionless conditions. Even strong infrared radiators require 10^{-3}–10^{-2} s to approach radiative equilibrium. This condition puts disastrous constraints on the total sample pressure allowable in a conventional gas bulb experiment. Furthermore, even if the sample pressure could be lowered enough without adverse effects of the concomitant loss of signal, the increasing rate of diffusion at lower pressure would introduce a new problem in measuring the inherently slow infrared radiative relaxation. This quenching diffusion

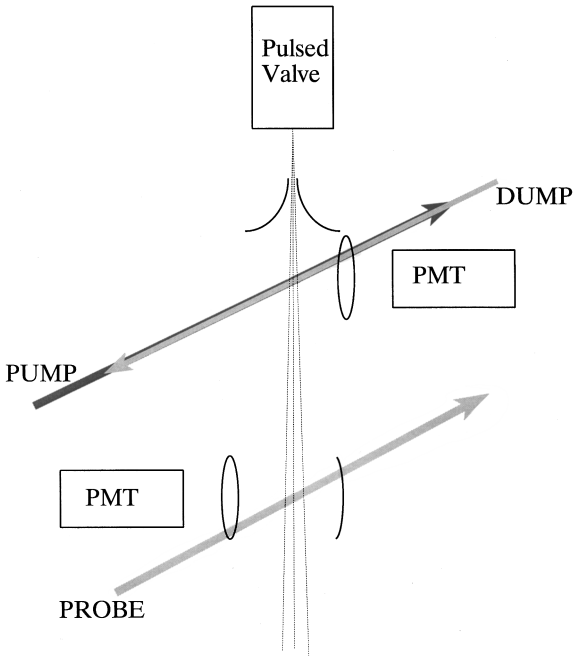

FIG. 1. A schematic diagram of an apparatus capable of measuring the time dependence of the infrared radiative decay under collision free conditions. The PUMP and DUMP laser beams prepare vibrationally excited NO in front of the upper phototube. After a collision free flight time of 80.9 μs the population distribution, which is altered by infrared radiative relaxation, is probed by LIF in front of the lower phototube.

conundrum explains why direct measurement of infrared rates in the time domain is difficult.

This problem may be overcome by use of a molecular beam. Preparation of a highly concentrated sample of an individual quantum state of a vibrationally excited molecule is thereby possible under collision free conditions. The sample can then be transported without collisions to an optimized detection region. Since few of the molecules are lost in transport, the sample can be probed under optimum conditions many μs after preparation. The pristine conditions of the molecular beam allow the observation of the radiative relaxation of the vibrationally excited sample absent the effects of collisions.

EXPERIMENT

The apparatus is shown schematically in Fig. 1. A collimated pulsed molecular beam was formed by expanding 5 atm of NO from a 0.8 mm orifice (General Valve®) and skimming with a 2.0 mm diam electro-formed skimmer 3 cm downstream. SEP was performed at the preparation zone of the machine 6 cm below the nozzle. To accomplish SEP two lasers were used. The output of an argon ion (Spectra Physics 171®) pumped single-mode ring dye laser (Coherent CR-699®) operating on R6G was pulse amplified in a three-stage home-built dye (R610) amplifier by a frequency doubled Q-switched, injection-seeded Nd:YAG laser (Continuum 7010-IS®), which had a pulse energy of 400 mJ at 532 nm and a pulse duration of 5 ns. The amplified ring laser radiation possessed a pulse-energy of ~60 mJ and was frequency doubled in a KDP crystal to yield 15 mJ of UV radiation around 300 nm. After passing a 266 nm $\lambda/2$ plate, the frequency-doubled and residual fundamental laser beams were mixed in a BBO crystal to yield radiation near 200 nm with an energy of 1.5–2.5 mJ/pulse and a Fourier transform limited bandwidth of ~200 MHZ. This laser was used to pump individual Λ doublets of the $R_{11}(1.5)$ line in the $B(5 \text{ or } 4) \leftarrow X(0)$ band. An excimer pumped dye laser operating on C-153 was used to DUMP molecules to $X(21)$. By installing a KDP crystal, the doubled output could also be used to DUMP through the $B(4) \rightarrow X(7)$ band. LIF and fluorescence-dip measurements could be carried out using a PMT installed to image the preparation zone of the experiment.

Some 6.35 cm further downstream, a second excimer pumped dye laser operating on C-153 was used to perform LIF on the radiatively relaxing molecular sample. The $B(5) \leftarrow X(20)$, $B(4) \leftarrow X(19)$, $B(3) \leftarrow X(18)$, as well as $B(2) \leftarrow X(17)$ vibronic bands were used to this end. By installing a KDP doubling crystal, the $B(1) \leftarrow X(6)$, and $B(0) \leftarrow X(5)$ bands could also be reached. The laser induced fluorescence (LIF) was collected by a quartz F/0.7 lens system and imaged onto a solar blind phototube (Hamamatsu 166UH®). A spherical reflector was used to increase the collection efficiency of the optical system to ~25%. The signal of the photomultiplier was processed by a digital oscilloscope (LeCroy 9430®) and a boxcar integrator (SRS 250®) interfaced with a computer.

RESULTS

Figure 2 shows some of the results of this work. The upper panel was taken by scanning the PROBE laser, delayed 80.9 μs after the PUMP laser, in the vicinity of the $B(4) \leftarrow X(19)$ bandhead after preparation of $B(5)J=2.5$ with the PUMP laser and in the absence of the DUMP laser. The populated levels of $X(19)$ are $J=1.5$, 2.5, and 3.5 and are due to the spontaneous emission (Franck–Condon pumping) of the $B(5)$ state, which obeys the selection rules $\Delta J=0, \pm 1$. It can be seen that this parallel Π–Π transition favors $\Delta J=\pm 1$. The middle panel shows the effect of introducing the DUMP laser at the preparation zone of the machine and tuning it to the $P_{11}(3.5)$ transition of $B(5) \rightarrow X(21)$. The enhancement of the $v=19$ signal for $R(2.5)$, $Q(2.5 \text{ and } 4.5)$, as well as $P(2.5 \text{ and } 4.5)$ is observable. Less obvious is the decrease in the population of $J=1.5$ and 3.5, due to the large fraction of B-state population that is unavailable for spontaneous visible emission to $v=19$. Figure 2 presents experimental evidence of a process where NO loses two vibrational quanta but only $1\hbar$ of angular momentum. This is not consistent with collisions in the beam.

The bottom panel of Fig. 2 shows the difference signal of the upper and middle panel. This was obtained by triggering the DUMP laser at 5 Hz, while all other components of the experiment were triggered at 10 Hz. The SR250 Boxcar integrator was set to ''toggle mode'', where the difference of odd and even shots was integrated and averaged. If we define the difference signal for the $J=3.5$ population as $\Delta_{19,3.5}$ and

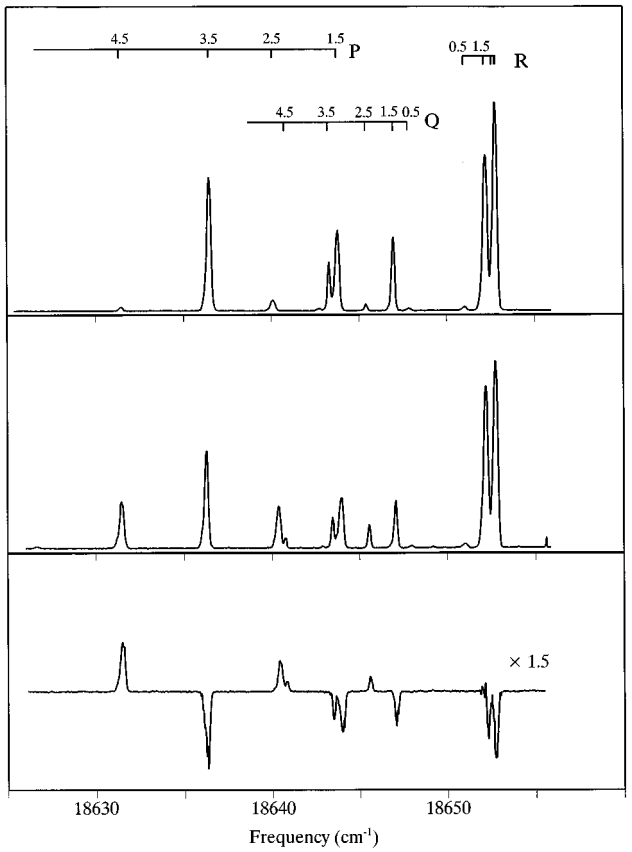

FIG. 2. Infrared emission's influence on the observed LIF spectra. Upper panel: The resulting probe spectrum of $v=19$ after the PUMP laser is tuned to the $R_{11}(1.5)$ line of the $B(5)\leftarrow X(0)$ band in the absence of the DUMP laser. Levels are populated by spontaneous emission from the $B\,^2\Pi$ state. Due to the selection rules of this ro-vibronic transition only $J=1.5$, 2.5, and 3.5 are observed. Middle panel: The resulting PROBE spectrum of $v=19$ with the DUMP laser populating $v=21$, $J=3.5$. Population observed in $J=4.5$ and 2.5 is seen to increase due to infrared emission between $v=21$ and $v=19$, which are governed by $\Delta J=\pm 1$ infrared selection rules. Bottom panel: difference of top two panels.

that of $J=4.5$ as $\Delta_{19,4.5}$, it can be shown that:

$$\frac{\Delta_{19,4.5}}{\Delta_{19,3.5}}=-\frac{fxn(21\rightarrow 19,3.5\rightarrow 4.5)}{fxn(5\rightarrow 19,2.5\rightarrow 3.5)},$$

where $fxn(21\rightarrow 19,3.5\rightarrow 4.5)$ is the fraction of molecules that have undergone the indicated infrared transition during the flight time and $fxn(5\rightarrow 19,2.5\rightarrow 3.5)$ is the fraction of molecules that have undergone the indicated electronic transition in the absence of the DUMP laser. In principle, this expression is approximate since the signal originating from $J=3.5$ results from some infrared emission as well. However in practice the infrared Q branch is $\sim 20x$ weaker than the observed P and R branches and thus, this contribution to the $J=3.5$ signal is smaller than the noise of the measurement. Likewise, $\Delta\Omega=+1$ infrared emissions are expected to be weak and could not be observed. Therefore the signal loss induced by the DUMP laser for $J=3.5$ is due entirely to the competition between stimulated emission to $v=21$ and spontaneous visible emission to $v=19$. In contrast the signal increase for $J=4.5$ is due entirely to the collaboration of stimulated visible emission to $v=21$ and spontaneous infrared emission from $v=21-19$. The fraction of B-state population depleted by the DUMP laser does not influence the experimental analysis. Similar ''toggle mode spectra'' were also obtained for the $B(5)\leftarrow X(20)$, $B(3)\leftarrow X(18)$, and $B(2)\leftarrow X(17)$ bands. This allowed the determination of the quantities: $fxn(21\rightarrow v'',\ 3.5\rightarrow 4.5)$, $fxn(21\rightarrow v'',\ 3.5\rightarrow 2.5)$ for $v''=20,19,18$, and 17. These results could be combined with the value of $fxn(5\rightarrow v'',\ 2.5\rightarrow 3.5)$ for $v''=20,19,18$, and 17 in order to obtain the extent of infrared radiation during the 80.9 μs. The quantity, $fxn(5\rightarrow v'',\ 2.5\rightarrow 3.5)$, the fraction produced in $J=3.5$ by Franck–Condon pumping could be calculated from known spectroscopic data on the $B-X$ emission system. To accomplish this a standard RKR analysis[24–26] was carried out to obtain the vibrational wave functions for the B and X electronic states. The semiempirical transition dipole moment function reported recently by Langhoff *et al.*[27] was fit to a fourth order polynomial damped by an exponential function to ensure smoothness and proper behavior in the asymptotic region. This fit function was used together with the wave functions to calculate the final state distribution produced by Franck–Condon pumping. A similar procedure was previously carried out and compared to quantitative emission spectroscopy from $v'=6$ of the $B\,^2\Pi$ state and was found to yield fractional populations due to spontaneous emission to an accuracy of about 10% for most transitions.[27] There is excellent agreement between this semiempirical transition dipole moment and that determined experimentally by Piper *et al.*[28]

TABLE I. Einstein A coefficients for highly vibrationally excited NO.

$v'\rightarrow v''$	This work (s^{-1})	Langhoff *et al.* (s^{-1})	Billingsley (s^{-1})
21→20	70.0±3.6[a] (69.9)[b]	63.9[c] (66.9)[d]	45[e]
21→19	66.7±3.4[a] (64.7)[b]	59.7[c] (61.2)[d]	65[e]
21→18	27.2±2.4[a] (22.2)[b]	24.5[c] (22.9)[d]	···
21→17	5.9±1.7[a,f] (9.4)[b]	··· (11.1)	···
7→6	55.7±6.8[a] (63.7)[b]	60.0[c] (58.8)[d]	53.5

[a]95% confidence intervals, based on statistical error analysis.
[b]Calculated from the EDMF derived in this work. See Table II.
[c]See Ref. 20. These values were derived using an *ab initio* potential curve as well as an *ab initio* EDMF.
[d]These values were derived by us using the EDMF of Ref. 20 and an accurate RKR potential curve.
[e]See Ref. 18. These calculations ended at $v=20$. The values in the table have been extrapolated from lower vibrational levels.
[f]Derived radiative lifetime for $v=21$, $J=3.5$, $\Omega=0.5$ is $5.89\pm 0.38\times 10^{-3}$ s.

Having the fraction that has undergone infrared radiation in a predetermined flight time allows the direct reduction of the data to infrared Einstein A coefficients. These results are shown in Table I for all of the bands measured in this work. These may be summed over final vibrational states to give the infrared radiative lifetime of the $X\,^2\Pi(v=21)$ level, which is found to be 5.9 ms. Also shown in this table are the results of *ab initio* calculations, where A coefficients for the theoretical rotationless level were reported.[20] Because of the weak dependence of A on J[29] the present results for $J=3.5$ are expected to be nearly identical to this quantity as well as rotationally averaged values reported in other work.[16–18] The

TABLE II. The electric dipole moment function of NO $X(^2\Pi)$.

Polynomial coefficient[a]	Least squares value[b]
μ_e	-0.16718 ± 0.00020[c]
c_1	2.251 ± 0.044
c_2	-1.452 ± 0.066
c_3	2.55 ± 0.95
c_4	-3.73 ± 1.66

[a] $\mu(r-r_e)\equiv\mu_e+c_1(r-r_e)+c_2(r-r_e)^2+c_3(r-r_e)^3+c_4(r-r_e)^4$, where r is the nuclear separation in Å and $r_e\equiv1.150\,64$ Å.
[b] The derived EDMF is expected to be accurate to within ±0.016 D between 0.9 and 1.7 Å.
[c] The minus sign indicates N^-O^+ polarity.

agreement between the results of this work and the most recent work of Langhoff *et al.* is nothing short of spectacular. This serves as clear confirmation that the new technique of SEP molecular beam time-of-flight determination of Einstein *A* coefficients is working as expected. The Einstein *A* coefficients derived from this work also clearly show that the ratio of first overtone-to-fundamental emission continues to rise above $v=11$, in agreement with *ab initio* results and in contrast to chemiluminescence experiments.[19] Also shown for comparison is the earlier *ab initio* calculation of Billingsley.[18] These calculations are clearly less reliable and suggest the EDMF function of that work is inaccurate.

For many problems in Aeronomy, the infrared Einstein *A* coefficients are necessary input data. The method demonstrated in this work gives a direct means for obtaining these rate constants, bypassing the sometimes cumbersome determination of the EDMF. If one is instead interested in the EDMF itself, measurements such as those shown in this paper are also quite useful. To demonstrate this we have carried out a least squares determination of the EDMF using the data from this work, the first overtone-fundamental emission branching ratio's for $v\leqslant11$[19] and the vibrational state specific dipole moments for $v=0$[30] and 1.[31] The resulting EDMF, represented as a fourth order polynomial expanded about the equilibrium bond length is shown in Table II. It reproduces the experimentally derived *A* coefficients within ~10%. This EDMF is within 0.04 D of Langhoff's *ab initio* calculation[20] between 0.9 and 1.7 Å. If the analysis is repeated using only the data from this work and the dipole moment of $v=0$, an EDMF is obtained which differs by less than 0.016 D within the same bond length range, which we take to be the uncertainty in the derived EDMF. The large amplitude motion of the high vibrational states is enough to fully sample the EDMF in this region. The resulting EDMF has been used to construct the Einstein $A_{v',v''}$ rate constant matrix which has been archived.[32]

CONCLUSION AND OUTLOOK

In light of the complete absence of direct measurement of the *rates* of infrared relaxation for small molecules under collision free conditions, other experiments are indicated. For example, this method could be applied to the OH Meinel emission problem,[33,34] at least up to $v=4$. The infrared emission rates of this molecule have been worked out in an analogous way to those of NO, albeit the data set is of much higher quality as this problem has received much greater attention than NO. The infrared emission rates of CO are also important, as they govern the kinetics of the CO chemical laser and have astrophysical significance. This molecule could also be tackled with SEP, molecular beam time-of-flight.

In conclusion, we have presented the first experiments which monitor the collision free infrared radiative relaxation rates for neutral molecules.[35] We have shown that for molecules where stimulated emission pumping is possible, the infrared emission rates of the ground electronic states can be calibrated against the UV–visible emission rates of a well characterized excited electronic state. The question comes to mind if the approach could be decoupled from the Franck–Condon pumping. One way would be to introduce a fourth laser! By saturating the infrared transition with a cw laser in the preparation zone, a known fractional population transfer could be created, which would be determined by the ratio of degeneracies of upper and lower levels brought into radiative equilibrium with one another by the infrared laser. The signal detected in the PROBE region of the machine could then be used to compare with that detected from *spontaneous* infrared emission, that is, in the absence of the infrared laser. In this way, the fraction of population that underwent spontaneous infrared emission during a well defined flight time could be determined without the knowledge of the radiative rates of the excited electronic state used in the SEP. Indeed for such an arrangement, vibrational pumping schemes other than SEP could be employed. For example, overtone pumping of OH could provide an avenue to direct time-dependent measurement of the important Meinel system.

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